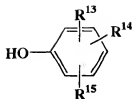


- dodecyl, tetradecyl, hexadecyl, octadecyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like.
- 5 The alkyl-substituted phenyl group is exemplified by dimethylphenyl, diethylphenyl, trimethylphenyl, methylethylphenyl and the like. The halogen-substituted phenyl group is exemplified by dichlorophenyl and the like. The alkyl-substituted benzyl group is exemplified by methylbenzyl,
- 10 dimethylbenzyl, diethylbenzyl,  $\alpha$ -methylbenzyl and the like. The halogen-substituted benzyl group is exemplified by chlorobenzyl, dichlorobenzyl and the like. As  $R^{12}$ , ethyl, butyl, diethylphenyl, methylethylphenyl, benzyl are preferable.
- Specific examples of 2,3-dichloromaleimides of the
- 15 formula (12) include 2,3-dichloro-N-ethylmaleimide, 2,3-dichloro-N-isopropylmaleimide, 2,3-dichloro-N-n-butylmaleimide, 2,3-dichloro-N-tert-butylmaleimide, 2,3-dichloro-N-n-octylmaleimide, 2,3-dichloro-N-cyclohexylmaleimide, 2,3-dichloro-N-benzylmaleimide, 2,3-dichloro-N-(2-
- 20 chlorobenzyl)maleimide, 2,3-dichloro-N-(4-chlorobenzyl)maleimide, 2,3-dichloro-N-(2-methylbenzyl)maleimide, 2,3-dichloro-N-(2,4-dimethylbenzyl)maleimide, 2,3-dichloro-N-(3,4-dimethylbenzyl)maleimide, 2,3-dichloro-N- $\alpha$ -
- 25 methylbenzylmaleimide, 2,3-dichloro-N-(2,4-dichlorobenzyl)maleimide, 2,3-dichloro-N-(2-ethyl-6-methylphenyl)maleimide, 2,3-dichloro-N-(2,6-dimethylphenyl)maleimide, 2,3-dichloro-N-(2,6-diethylphenyl)maleimide, 2,3-dichloro-N-(2,4-
- 30 diethylphenyl)maleimide, 2,3-dichloro-N-(2,4,6-trimethylphenyl)maleimide and the like.

There are also mentioned phenols of the formula (13):



(13)

wherein  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are the same or different and each is hydrogen atom, alkyl group, halogen-substituted alkyl group, cycloalkyl group, phenyl group, halogen atom, alkoxy group, carboxyl group, alkenyl group or aralkyl group.

In the formula (13), the alkyl group at  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  is exemplified by straight or branched chain alkyl having 1 to 9 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, nonyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like. The halogen atom is exemplified by fluorine atom, chlorine atom, bromine atom and iodine atom. The alkoxy group is exemplified by straight or branched chain alkoxy having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and the like. The alkenyl group is exemplified by straight or branched chain alkenyl having 2 to 4 carbon atoms such as vinyl, allyl, isopropenyl and the like. The aralkyl group is exemplified by aralkyl having 7 to 9 carbon atoms such as benzyl, cumyl and the like. As  $R^{13}$ ,  $R^{14}$  and  $R^{15}$ , hydrogen atom, fluorine atom, chlorine atom, methyl, ethyl, t-butyl, nonyl and vinyl are preferable.

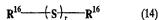
Specific examples of phenols of the formula (13) include nonylphenol, cumylphenol, 4,6-ditert-butyl-m-cresol, 1-cyclohexyl-5-methylphenol, 2,6-ditert-butyl-p-cresol, 2-phenylphenol, 2-butyl-6-ethyl-4-isopropylphenol, cyclohexyl-5-methylphenol, 2-bromo-6-chloro-4-dichloromethylphenol, 2-fluoro-4-iodo-3-trichloroethylphenol, 3-hydroxy-5-methoxybenzoic acid, 4-ethoxy-2-vinylphenol and the like.

Preferred antifouling component mentioned above other than the polymer containing triphenylboron (1), (2) or (3)

includes bis(2-pyridylthio-1-oxide)zinc, bis(2-pyridylthio-1-oxide)copper, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, cuprous oxide, copper thiocyanate (CuSCN), N,N-dimethyldichlorophenyl urea, 4,5-dichloro-2-n-octyl-3-isothiazolone, N-(fluorodichloromethylthio)phthalimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, zinc dimethyldithiocarbamate, bis(dimethyldithiocarbamoyl)zinc ethylene bisdithiocarbamate, pyridine-triphenylboron, triphenylboron-alkyl(3-30 carbon atoms)amine (e.g., triphenylboron-n-octadecylamine, triphenylboron-n-hexadecylamine, triphenylboron-n-octylamine and the like), triphenylboron-rosin amine, copper rhodanide and tetraethyl thiuram disulfide.

The above-mentioned antifouling component other than the polymer containing triphenylboron (1), (2) or (3) may be used alone or in combination of two or more kinds thereof. The weight ratio of the above-mentioned antifouling component other than the polymer containing triphenylboron (1), (2) or (3) to the polymer containing triphenylboron (1), (2) or (3) of the present invention can be optionally changed according to the environment of application, which is preferably 1:50-50:1, more preferably 1:25-25:1, particularly preferably 1:10-10:1. When the content of the above-mentioned antifouling component is greater than the above-mentioned range, the property of a coating film is degraded and when it is smaller conversely, an effect afforded by concurrent use is not expected.

The elution regulator to be used for the fishnet antifouling agent of the present invention is exemplified by dialkyl polysulfides of the formula (14):



wherein each  $R^{16}$  is the same or different and is alkyl group having 1 to 20 carbon atoms and r is an integer of 2-10.

In the formula (14), the alkyl group having 1 to 20 carbon atoms at  $R^{16}$  is preferably exemplified by straight or branched chain alkyl having 2 to 19 carbon atoms, such as ethyl, propyl, t-butyl, t-amyl, t-nonyl, t-dodecyl, nonadecyl and the like and r is preferably 3 to 8.

Specific examples of dialkyl polysulfides of the formula (14) include diethyl pentasulfide, dipropyl tetrasulfide, di-tert-butyl disulfide, di-tert-butyl tetrasulfide, di-tert-amyl tetrasulfide, di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, di-tert-dodecyl pentasulfide, dinonadecyl tetrasulfide and the like.

In addition, polybutene having an average molecular weight of 200-1,000, paraffins, petrolatum, glycerin, polyhydric alcohols and fatty acid esters can be used as an elution regulator.

Examples of polybutene having an average molecular weight of 200-1,000 include LV-5, LV-10, LV-25, LV-50, LV-100, HV-15, HV-35, HV-50, HV-100, HV-300 manufactured by NIPPON OIL COMPANY, LTD. and the like. Examples of paraffins include liquid paraffin, paraffin wax, paraffin chloride and the like. Examples of petrolatum include white petrolatum, yellow petrolatum and the like.

Preferable examples of the above-mentioned elution regulator include di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, polybutene, liquid paraffin, white petrolatum and yellow petrolatum.

The above-mentioned elution regulator may be used alone or in combination of two or more thereof. The content of the above-mentioned elution regulator can be optionally changed according to the environment of application, which is preferably 1-30 wt%, more preferably 3-20 wt%, particularly preferably 5-10 wt%, in a fishnet antifouling agent. When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 30 wt%, it

unpreferably degrades property of a coating film.

B. Underwater antifouling coating

The underwater antifouling coating of the present invention shows low toxicity, is highly safe and shows a superior adhesion-preventive effect against coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, *Serpula* etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms for a long time.

The underwater antifouling coating of the present invention can be prepared by adding a polymer containing triphenylboron (1), (2) or (3) in water-soluble resin or non-water-soluble resin, and mixing and dispersing them using a paint conditioner, homomixer and the like. In addition, an additive such as other component generally used for coating, solvent (xylene, methyl isobutyl ketone, n-butanol, butyl acetate etc.), pigment (red iron oxide, titanium oxide, zinc oxide etc.), plasticizer, filler (talc, fine silica etc.), curing promoter and the like can be mixed as necessary.

The content of the polymer containing triphenylboron (1), (2) or (3) in the underwater antifouling coating of the present invention can be optionally changed according to the environment of application, which is preferably 1 wt% - 80 wt%, more preferably 3 wt% - 40 wt%. When the content is less than 1 wt%, an adhesion-preventive effect against aquatic fouling organisms becomes insufficient, and conversely, when it exceeds 80 wt%, it increases the viscosity of the coating, which unpreferably makes handling difficult.

When the polymer containing triphenylboron (1), (2) or (3) of the present invention is used as an underwater antifouling agent, a superior adhesion-preventive effect against aquatic fouling organisms can be achieved even by this polymer alone, but addition of silicone oil, elution regulator,

an antifouling component other than a polymer containing triphenylboron (1), (2) or (3) and the like allow exhibition of a more superior adhesion-preventive effect. Silicone oil, elution regulator, the antifouling components other than a  
5 polymer containing triphenylboron (1), (2) or (3) and the like include those exemplified for fishnet antifouling agent. Where necessary, various resins explained with regard to the fishnet antifouling agent can be also added.

The content of the silicone oil can be optionally  
10 changed according to the environment of application, which is preferably 0.1 - 50 wt%, more preferably 0.5 - 25 wt%, in an underwater antifouling coating. When the content is less than 0.1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 50 wt%, it unpreferably  
15 degrades property of a coating film.

The weight ratio of the antifouling component other than the polymer containing triphenylboron (1), (2) or (3) to the polymer containing triphenylboron (1), (2) or (3) of the present invention can be optionally changed according to the  
20 environment of application, which is preferably 1:50 - 50:1, more preferably 1:25 - 25:1, particularly preferably 1:10 - 10:1. When the above-mentioned antifouling component is greater than the above-mentioned range, the property of a coating film is degraded, and conversely, when it is lower, an  
25 effect afforded by concurrent use is not expected undesirably.

The content of the elution regulator can be optionally changed according to the environment of application, which is preferably 1 - 30 wt%, more preferably 3 - 20 wt%, particularly preferably 5-10 wt%, in an underwater antifouling coating.  
30 When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 30 wt%, it unpreferably degrades property of a coating film.

#### Examples

The present invention is explained in detail in the

following by way of Examples and Comparative Examples. It is needless to say that the present invention is not limited by these Examples. In the Examples, the contents are in wt%. In the Tables, triphenylboron is abbreviated as TPB.

5 Example 1 <synthesis of triphenylboron adduct>

Into a four neck 1 L flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed an aqueous solution of sodium hydroxide adduct of triphenylboron (250.3 g, 9% aqueous solution, manufactured by  
10 Tokyo Kasei Co., Ltd.) and stirring was started. Ethylene diamine (4.81 g, manufactured by Tosoh Corporation) was dropwise added at room temperature from the dropping funnel. After the dropwise addition, the mixture was stirred at the same temperature for 5 hr. The precipitate was collected by  
15 filtration and washed with water and dried to give white powdery substance (21.64 g). The obtained compound was subjected to elemental analysis and IR (infrared) spectrum analysis. As a result, the compound was confirmed to be a triphenylboron-ethylenediamine adduct (triphenylboron adduct A)  
20 of the objective substance, m.p. 157.8-159.8°C.

Examples 2-4 <synthesis of triphenylboron adduct>

By synthesizing in the same manner as in Example 1 using the starting materials shown in Table 1, triphenylboron adducts B-D were obtained. They are shown in Table 1 together  
25 with triphenylboron adduct A. In Table 1, each figure is in g (gram).

Table 1 triphenylboron adduct

(unit:g)

		Example			
		1	2	3	4
amine	Ethylenediamine	4.81			
	Propylenediamine		5.93		
	p-phenylene-diamine			8.65	
	4-aminopyridine				7.53
TPB-NaOH adduct *1		250.3	250.3	250.3	250.3
Yield		21.64	21.38	24.21	24.28
Adduct reference		A	B	C	D

\*1: sodium hydroxide adduct of triphenylboron, 9% aqueous solution

5

#### Example 5 <synthesis of polymers containing triphenylboron (1)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a solution (100 g) of methacrylic acid/methyl  
 10 methacrylate/2-ethylhexyl acrylate copolymer (resin 1, Mw=ca 10,000, acid value 18.6 mg KOH/g) in 40% xylene/n-BuOH, and stirring was initiated. The triphenylboron-ethylenediamine adduct (triphenylboron adduct A, 10.1 g) synthesized in Example 1 was cast in at room temperature and then xylene (16.1 g) was  
 15 added. The mixture was stirred at the same temperature for 5 hr to give a solution (polymer solution A, 126 g) of a polymer containing triphenylboron in xylene. The solvent was evaporated under reduced pressure from a part of the xylene solution and the residue was dried to give a pale-yellow white  
 20 resin like substance. By IR (infrared) spectrum analysis, it was confirmed to be the objective substance. The weight average molecular weight was about 13,000 (GPC). The IR (infrared) spectrum of this polymer is shown in Fig. 1.

#### Examples 6-15 <synthesis of polymers containing triphenylboron (1) and (2)>

25

In the same manner as in Example 5 using a triphenylboron adduct, a carboxyl group-containing polymer and a solvent shown



in Table 2, solutions of polymer containing a triphenylboron (polymer solutions B-K) were synthesized. They are collectively shown in Table 2 together with the polymer solution A. Unless particularly indicated, each figure in  
s Table 2 is in g (gram).

Table 2 polymer containing triphenylboron

(unit: g unless specifically indicated)

	TPB adduct	Example													
		5	6	7	8	9	10	11	12	13	14	15			
	adduct A	10.1	12.6	10.5	16.1	10.5									
	adduct B						11.9	13.2							
	adduct C								11.6	14.6					
	adduct D														
carboxyl group-containing polymer	Resin 1	100.0					100.0						11.2	14.0	
	Resin 2		20.0					20.0		20.0			100.0		
	Resin 3			20.0											20.0
	Resin 4				20.0										
	Resin 5					50.0									
	solvent	16.1	48.9	45.8	54.2	90.8	18.9	49.7	18.4	51.9	17.8				51.0
	yield (g)	126.0	81.2	76.0	90.0	151.0	130.3	82.4	130.0	86.2	129.0				86.0
	heating residue (%)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0				40.0
	weight average molecular weight ( $\times 10^4$ )	1.3	1.6	1.8	8.2	1.4	1.4	1.7	1.5	1.7	1.4				1.7
	basic constituting unit (%)	25.6	47.7	44.1	57.1	21.5	26.2	47.4	27.9	50.9	27.2				50.0
	TPB content (%)	16.1	30.9	27.7	35.8	13.9	15.9	29.6	15.6	29.2	15.7				29.7
	polymer solution reference	A	B	C	D	E	F	G	H	I	J	K			

Resin 1: methacrylic acid/methyl methacrylate/2-ethylhexyl acrylate copolymer (solid content 40%, acid value 18.6 mg KOH/g)

Resin 2: ethylene/acrylic acid (15 wt%) copolymer

Resin 3: ethylene/methacrylic acid (15 wt%) copolymer

Resin 4: t-butyl acrylate/ethyl acrylate/methacrylic acid (23 wt%) copolymer

Resin 5: ethylene/acrylic acid (10 wt%, about 50% Zn salt) copolymer

solvent: xylene alone or xylene/nBuOH mixed system

Examples 16-29 and Comparative Examples 1-3 <Formulation  
Examples of fishnet antifouling agents>

The fishnet antifouling agents of the present invention (Examples 16-29) were prepared in the compositions shown in  
5 Table 3 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, fishnet antifouling agents of Comparative Examples 1-3 were prepared. Each figure in Table 3 is in wt%.

Table 3 fishnet antifouling agent

Component	Composition (wt%)																				
	Example																		Comparative Example		
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	1	2	3				
Polymer solution	A	51.6	51.6	51.6	51.6																
	B				26.8																
	C					30.0															
	D						23.2														
	E							59.6													
	F								52.1												
	G									28.0											
	H										53.2										
	I											28.4									
	J												52.8								
	K													27.9							
TET															10.0						
PK																					
TNPS			5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0				
LV-50				5.0											5.0	5.0	5.0				
LR-155																					
silicone oil		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0							
xylene	48.4	44.4	39.4	34.4	64.2	61.1	67.9	31.4	38.9	63.0	37.8	62.6	38.3	63.1	60.0	60.0	70.0				

TET: tetraethyl thiuram disulfide

PK: triphenylboron-pyridine adduct

TNPS: di-t-nonyl polysulfide (maximum value of occupation 5)

LV-50: polybutene (Nippon Petrochemicals Co., Ltd.)

LR-155: acrylic resin (50% xylene solution, Mitsubishi Rayon Co., Ltd.)

silicone oil: polyether modified silicone oil

Examples 30-44 and Comparative Examples 4-7 <Formulation  
Examples of ship bottom antifouling coatings>

The ship bottom antifouling coating of the present invention (Examples 30-44) were prepared in the compositions  
5 shown in Table 4 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, ship bottom antifouling coatings of Comparative Examples 4-7 were prepared. Each figure in Table 4 is in wt%.

Table 4 ship bottom antifouling coating

component	Coating composition (wt%)																											
	Example																											
	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	4	5	6	7	Comparative Example								
polymer solution	50	50																										
	A																											
	B		50																									
	C			50																								
	D				50																							
	E					50																						
	F						50	50																				
	G								50																			
	H									50	50																	
	I											50																
	J																											
K																												
pigment	zinc oxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	red oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	colloidal silica	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
	talc	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	
	cuprous oxide	10																										
known polluting component	PK																											
	TPB-8																											
	vinyl resin																											
resin	varnish																											
	chlorinated isoprene rubber																											
solvent	xylene	15	5	15	15	15	15	5	15	15	5	15	15	5	15	15	15	15	15	15	15	15	15	15	15	15	15	
	MTBK	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	BuOH	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
	PK: triphenylboron-pyridine adduct, MTBK: methyl isobutyl ketone																											
TPB-8: triphenylboron-n-octylamine adduct, BuOH: n-butanol																												

Experimental Examl 1 <fishnet antifouling agent effect test>

The fishnet antifouling agents of Examples 16-29 and Comparative Examples 1-3 were respectively applied to polyethylene unknotted nets (6 knot, 400 denier/60 yarns) by immersion, air-dried and set on a metal frame. The test nets were retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken and the degree of fouling due to adhesion of aquatic fouling organisms was observed. The degree of fouling was evaluated according to the following criteria, the results of which are shown in Table 5.

Table 5 fishnet antifouling agent effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	16	A	A	A	A	B	B
	17	A	A	A	A	A	A
	18	A	A	A	A	A	A
	19	A	A	A	A	A	A
	20	A	A	A	A	A	A
	21	A	A	A	A	A	A
	22	A	A	A	A	A	A
	23	A	A	A	A	A	A
	24	A	A	A	A	A	A
	25	A	A	A	A	A	A
	26	A	A	A	A	A	A
	27	A	A	A	A	A	A
	28	A	A	A	A	A	A
	29	A	A	A	A	A	A
Comparative Example	1	C	D				
	2	A	A	A	B	C	D
	3	D					
untreated		D					

untreated: polyethylene unknotted net not treated with fishnet antifouling agent

15 Evaluation criteria of degree of fouling of net

Evaluation A: Area of fouling of fishnet, 0%, no adhesion of aquatic fouling organisms.

Evaluation B: Area of fouling of fishnet, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

Evaluation C: Area of fouling of fishnet, 10% to less than 50%,  
great amount of adhesion of aquatic fouling  
organisms, unpractical as a fishnet.

Evaluation D: Area of fouling of fishnet, 50% or more,  
5 markedly greater amount of adhesion of aquatic  
fouling organisms.

A number of aquatic fouling organisms such as barnacle  
and *Hydroides norvegica* adhered to the nets of Comparative  
Examples 1-3 and untreated nets in 1 to 4 months. On the other  
10 hand, shellfish, tubicolous polychaetes or other aquatic  
fouling organisms did not adhere at all to the nets of Examples  
16-29 retained underwater for at least 4 months.

Experimental Example 2 <ship bottom antifouling coating  
effect test>

15 The ship bottom antifouling coatings of Examples 30-44  
and Comparative Examples 4-7 were applied on both sides of 50×  
100×2 mm hard vinyl chloride plates to achieve a dry film  
thickness of about 100 micron. After air-drying for one day,  
these test plates were retained at about 1.5 meters underwater  
20 in the sea off Shukumo-shi, Kochi-ken and the degree of  
fouling of the test plates due to adhesion of aquatic  
organisms was observed. The degree of fouling was evaluated  
according to the following criteria, the results of which are  
shown in Table 6.

25



Table 6 ship bottom antifouling coating effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	30	A	A	A	A	A	A
	31	A	A	A	A	A	A
	32	A	A	A	A	A	A
	33	A	A	A	A	A	A
	34	A	A	A	A	A	A
	35	A	A	A	A	A	A
	36	A	A	A	A	A	A
	37	A	A	A	A	A	A
	38	A	A	A	A	A	A
	39	A	A	A	A	A	A
	40	A	A	A	A	A	A
	41	A	A	A	A	A	A
	42	A	A	A	A	A	A
	43	A	A	A	A	A	A
	44	A	A	A	A	A	A
Comparative Example	4	A	A	A	B	B	C
	5	A	B	C	C	D	
	6	A	B	B	C	D	
	7	A	B	C	D		
untreated		D					

untreated: hard vinyl chloride plates not treated with ship  
bottom antifouling coating

5 Evaluation criteria of degree of fouling of test plate

Evaluation A: Area of fouling of test plate, 0%, no adhesion  
of aquatic fouling organisms.

10 Evaluation B: Area of fouling of test plate, over 0% to less  
than 10%, small amount of adhesion of aquatic  
fouling organisms to the extent practically  
acceptable.

15 Evaluation C: Area of fouling of test plate, 10% to less than  
50%, great amount of adhesion of aquatic fouling  
organisms, impractical as a ship bottom  
antifouling coating.

Evaluation D: Area of fouling of test plate, 50% or more,  
markedly greater amount of adhesion of aquatic  
fouling organisms.

A number of aquatic fouling organisms such as barnacle

and *Hydroides norvegica* adhered to the plates of Comparative Examples 4-7 and untreated plates in 1 to 4 months. On the other hand, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the plates of

5 Examples 30-44 retained underwater for 6 months.

Example 45 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed poly(4-vinylpyridine) (5.3 g, reagent of Aldrich,

10 molecular weight about 60,000) dissolved in methanol (50 g) and stirring was started. The temperature of the system was raised to 50°C, an aqueous solution (157,g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was added dropwise from the dropping funnel over

15 about 1 hr. After the completion of the dropwise addition, the mixture was stirred at the same temperature for 1 hr. The solvent was evaporated under reduced pressure and water was added. The precipitated viscous insoluble material was collected by filtration, washed with water and dried to give 14

20 g of a pale-yellowish white polymer substance (polymer A).

The obtained compound was subjected to IR (infrared) spectrum analysis. As a result, the compound was confirmed to be the objective substance. The IR (infrared) spectrum thereof is shown in Fig. 2. In addition, the weight average molecular

25 weight was measured by gel permeation chromatography (GPC) and found to be about 198,000. The content of triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer A were 85 wt% and 59 wt%, respectively.

30 Example 46 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed 4-vinylpyridine-butyl methacrylate copolymer (5.3 g, reagent of Aldrich, butyl methacrylate content 10 wt%)

dissolved in methanol (50 g) and stirring was started. The temperature of the system was raised to 50°C, an aqueous solution (142 g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was added dropwise from the dropping funnel over about 1 hr. After the completion of the dropwise addition, the mixture was stirred at the same temperature for 1 hr. The solvent was evaporated under reduced pressure and water was added. The precipitated viscous insoluble material was collected by filtration, washed with water and dried to give 12.3 g of a pale-yellowish white polymer substance (polymer B). The content of triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer B were 78 wt% and 54 wt%, respectively.

15 Example 47 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a 49 wt% xylene solution (28.3 g) of 4-vinylpyridine-butyl methacrylate copolymer (4-vinylpyridine content 10 wt%) and stirring was started. The temperature of the system was raised to 50°C, and an aqueous solution (37.0 g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was added dropwise from the dropping funnel over about 30 min. After the completion of the dropwise addition, the mixture was stirred at the same temperature for 2 hr. The reaction mixture was transferred to a partition funnel and left standing. The aqueous layer was partitioned and water was added to the xylene layer and washed. Washing was repeated until the partitioned aqueous layer did not show alkalinity, and the solvent was evaporated under reduced pressure to give 15.5 g of a yellow-brown resin-like substance (polymer C). The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 140,000. The content of the triphenylboron-containing

constituting unit of the formula (3) and the content of triphenylboron in polymer C were 14.3 wt% and 10.0 wt%, respectively.

Example 48 <synthesis of polymer containing triphenylboron (3)>

5 Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a 45 wt% xylene solution (46.7 g) of 4-vinylpyridine-zinc methacrylate copolymer (4-vinylpyridine content 5 wt%) and stirring was started. The temperature of the system was  
10 raised to 50°C, and triphenylboron (2.5 g, reagent of Aldrich) was added by small portions. After the completion of the addition, the mixture was stirred at the same temperature for 2 hr. The solvent was evaporated under reduced pressure to give 21.0 g of a yellow-brown resin-like substance (polymer D).  
15 The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 3,000. The content of the triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer D were 11.8 wt% and 8.2 wt%, respectively.

20 Examples 49-52 and Comparative Examples 8-9 <Formulation Example of fishnet antifouling agent>

The fishnet antifouling agents of the present invention (Examples 49-52) were prepared in the compositions shown in Table 7 using the polymers A-D obtained in Examples 45-48. In  
25 the same manner, fishnet antifouling agents of Comparative Examples 8-9 were prepared. Each figure in Table 7 is in wt%. The polybutene used was LV-50 (manufactured by Nippon Petrochemicals Co., Ltd.), and the acrylic resin (50% xylene solution) was LR-155 (manufactured by Mitsubishi Rayon Co.,  
30 Ltd.).

Table 7 fishnet antifouling agent

(unit: wt%)

component	Example 49	Example 50	Example 51	Example 52	Comparative Example 8	Comparative Example 9
polymer A	10					
polymer B		10				
polymer C			30			
polymer D				30		
acrylic resin (50% xylene solution)	20	20			20	20
xylene	70	70	70	70	60	60
pyridine-triphenylboron						10
tetraethylthiuram disulfide					10	
polybutene					5	5
yellow petrolatum					5	5

5 Experimental Example 3 <fishnet antifouling agent effect test>

The fishnet antifouling agents of Examples 49-52 and Comparative Examples 8-9 were respectively applied to polyethylene unknotted nets (6 knots, 400 denier/60 yarns) by immersion, air-dried and retained at about 1.5 meters

10 underwater in the sea off Shukumo-shi, Kochi-ken, for 6 months from April 1998. The nets were pulled out every month and the degree of fouling was evaluated for 6 months according to the following criteria, the results of which are shown in Table 8.

Evaluation criteria of degree of fouling of net

15 Evaluation A: Area of fouling of fishnet, 0%, no adhesion of aquatic fouling organisms.

Evaluation B: Area of fouling of fishnet, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

20 Evaluation C: Area of fouling of fishnet, 10% to less than 50%,

great amount of adhesion of aquatic fouling organisms, often unusable as a fishnet.

Evaluation D: Area of fouling of fishnet, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms, unusable as fishnet.

Table 8 fishnet antifouling agent effect test results

	1 month	2 month	3 month	4 month	5 month	6 month
Example 49	A	A	A	A	B	B
Example 50	A	A	A	A	B	B
Example 51	A	A	A	A	B	B
Example 52	A	A	A	A	A	A
Comparative Example 8	C	D				
Comparative Example 9	A	A	A	B	C	C
untreated net	D					

untreated net: polyethylene unknotted net not treated with fishnet antifouling agent

- 10 A number of aquatic fouling organisms such as barnacle and *Hydroides norvegica* adhered to the nets of Comparative Example 8 and untreated nets in 1 to 2 months. while adhesion of aquatic fouling organisms to the net of Comparative Example 9 was not found in 3 months, they started to adhere in 4 months.
- 15 In contrast, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the nets of Examples 49-52 retained underwater for 4 months.

Examples 53-64 and Comparative Examples 10-15 <Formulation Example of underwater antifouling coating>

- 20 The underwater antifouling coating (Examples 53-64 and Comparative Examples 10-15) were prepared in the compositions shown in Table 9 by mixing each component.

Table 9 underwater antifouling coating

Component	Component	Coating composition (wt%)																	Comparative Example				
		Example																					
		53	54	55	56	57	58	59	60	61	62	63	64	10	11	12	13	14	15				
resin	vinyl resin	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30				
	varnish-chlorinated isoprene rubber	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10				
pigment	zinc oxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10				
	red oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5				
	colloid-silica	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3				
	talc	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10				
	polymer A	10	5	5																			
	polymer B			10	5	5																	
anti-fouling active ingre-	polymer C						10	5	5														
	polymer D									10	5	5											
di-	PK													10	5	5							
	TPB-8																10	5	5				
	cuprous oxide		10			10		10				10			10			10					
	copper rhodanide			10			10			10				10		10			10				
organic solvent	xylene	15	10	10	15	10	10	15	10	10	15	10	10	10	10	10	10	10	10				
	MTBK	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5				
	n-butyl alcohol	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2				

PK: pyridine-triphenylboron, TPB-8: triphenylboron-n-octylamine, MIBK: methyl isobutyl ketone

Experimental Example 4 <underwater antifouling coating effect test>

- A typical anticorrosive coating was applied to sandblasted steel plates in advance, and the coatings of
- 5 Examples 53-64 and Comparative Examples 10-15 were applied twice with a brush on the dry film to prepare test plates (100 mm × 300 mm) having an underwater antifouling coating having a dry coating film thickness of about 100 μm. These test plates were retained at about 1.5 meters underwater in the Shukumo
- 10 gulf, Shukumo-shi, Kochi-ken, for 12 months, and the degree of adhesion of aquatic fouling organisms was observed every 3 months during this period. The degree of adhesion of the aquatic fouling organisms was evaluated according to the following criteria, the results of which are shown in Table 10.
- 15 Evaluation criteria of degree of adhesion of aquatic fouling organisms

- No adhesion of aquatic fouling organisms   ◎
- Area of adhesion of aquatic fouling organisms  
less than 10%   ○
- 20 Area of adhesion of aquatic fouling organisms  
10% - less than 20%   △
- Area of adhesion of aquatic fouling organisms  
20% - less than 30%   ×
- Area of adhesion of aquatic fouling organisms
- 25 30% or above   ××



Table 10 underwater antifouling coating effect test results

adhesion-preventive effect				
	3 month	6 month	9 month	12 month
Example 53	⊙	⊙	⊙	⊙
Example 54	⊙	⊙	⊙	⊙
Example 55	⊙	⊙	⊙	⊙
Example 56	⊙	⊙	⊙	⊙
Example 57	⊙	⊙	⊙	⊙
Example 58	⊙	⊙	⊙	⊙
Example 59	⊙	⊙	⊙	⊙
Example 60	⊙	⊙	⊙	⊙
Example 61	⊙	⊙	⊙	⊙
Example 62	⊙	⊙	⊙	⊙
Example 63	⊙	⊙	⊙	⊙
Example 64	⊙	⊙	⊙	⊙
Comparative Example 10	⊙	⊙	○	○
Comparative Example 11	△	×	××	××
Comparative Example 12	△	×	××	××
Comparative Example 13	⊙	⊙	○	○
Comparative Example 14	△	×	××	××
Comparative Example 15	△	×	××	××

As is evident from Table 10, the test plates coated with the coatings of Comparative Examples 10-15 showed a decreased  
 5 adhesion-preventive effect in 3-9 months of immersion. In contrast, the test plates coated with the coatings of Examples 53-64 did not show adhesion of aquatic fouling organisms even after 12 months of immersion in sea.

Example 65 <synthesis of triphenylboron-containing vinyl  
 10 monomer>

Into a four neck 500 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was

placed an aqueous solution (370 g, 9% aqueous solution, reagent of Tokyo Kasei Co., Ltd.) of sodium hydroxide adduct of triphenylboron and stirring was started at room temperature. Thereto was dropwise added 4-vinylpyridine (10.5 g, Koei Chemical co., Ltd.) over about 30 minutes. After the dropwise addition, the mixture was stirred at the same temperature for 2 hr. The precipitate white insoluble material was collected by filtration, washed with water and dried to give a white powder (34.9 g). The obtained compound was subjected to IR (infrared) spectrum analysis. As a result, the compound was confirmed to be a 4-vinylpyridine-triphenylboron adduct.

Example 66 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 500 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer were placed a triphenylboron-containing vinyl monomer (10 g) synthesized in Example 65, butyl methacrylate (90 g), xylene (100 g) and azobisisobutyronitrile (0.2 g), and the mixture was polymerized for 2 hr under a nitrogen atmosphere while maintaining the temperature at 80-90°C. Azobisisobutyronitrile (0.2 g) was further added at the same temperature and the mixture was polymerized for 2 more hours to give a polymer solution having a heating residue of 50.1%. The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 20,000. The content of the triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in the obtained polymer were 9.7 wt% and 6.9 wt%, respectively.

**Industrial Applicability**

As is evident from the foregoing explanation, the polymer containing triphenylboron (1), (2) or (3) of the present invention shows extremely small adhesion of coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, *Serpula* etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios*

*kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms and shows a superior adhesion-preventive effect for a long time. Because it has a function of not only an active ingredient but also a binder, the polymer characteristically  
5 shows fine miscibility with other coating resins and a less adverse influence on the environment. Therefore, a fouling preventive containing this polymer, such as a fishnet antifouling agent and an underwater antifouling coating (e.g., a ship bottom antifouling coating etc.), becomes extremely  
10 useful.

This application is based on patent application Nos. 1999-206799, 2000-76939 and 2000-80153 filed in Japan, the contents of which are hereby incorporated by reference.

15